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SPECIFIC HEAT MEASUREMENTS ON HIGH T_c A-15s

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Specific heat measurements for the seven high T_c A-15's are reviewed. Derivation of values for γ , proportional to $N(0)(1+\lambda)$, is discussed, with strict attention given to limits of error. Particular note is taken of recent controversies concerning the correct values of γ for A-15 V_3Si and Nb_3Sn . Using tunneling and infrared spectroscopy results for λ where available, and an approximate phenomenological formula otherwise, values for the electronic density-of-states at the Fermi energy, $N(0)$, are derived and compared with theory. These specific heat derived $N(0)$ values, ranging from 0.95 ± 0.3 states/eV-atom for A-15 Nb_3Si to 2.4 ± 0.3 states/eV-atom for A-15 V_3Si , are taken as conclusive evidence that high T_c does not imply a high $N(0)$.

INTRODUCTION

Since the discovery of high T_c superconductivity in A-15 V_3Si (Hardy and Hulm, 1954), compounds forming in the A-15 structure have been the subject of an intense research effort. In addition to the properties of A-15's which make them attractive technologically, i.e., high upper critical currents and fields, these compounds are extremely interesting from a basic physics point of view. This review article, as clear from the title, considers just one of the many types of measurement techniques used in trying to understand the basic physical properties of A-15 compounds. In addition, this discussion will concentrate mostly on that subset of specific heat measurements with which I am most familiar and which hold the most fascination for me, i.e., LTSH measurements on the high T_c ($T_c > 17.0K$) A-15's:

Nb_3Ge , $T_c = 22.5K$ (Harper et al., 1975; Stewart et al., 1978a);
 Nb_3Ga , $T_c = 20.3K$ (Stewart and Webb, 1980);
 Nb_3Al , $T_c = 18.8K$ (Willens et al., 1969; Spitzli, 1970; Junod et al., 1971);
 Nb_3Sn , $T_c = 18.0K$ (Morin and Maita, 1963; Vieland and Wicklund, 1968; Junod et al., 1978; Stewart et al., 1981a);
 Nb_3Si , $T_c = 18.0K$ (Stewart et al., 1981b; Stewart et al., 1981c);
 V_3Si , $T_c = 17.1K$ (Morin and Maita, 1963; Spitzli 1970; Junod et al., 1971);
 $Nb_3Al_{0.8}Ge_{0.2}$, $T_c = 20.0$ (Matthias et al., 1967; Bohmhammel et al., 1977; Stewart et al., 1978b).

Even this relatively narrow topic, the LTSH of only seven A-15 compounds, with data stretching back almost two decades, is still full of controversy, uncertainty, and vigor. This review article attempts to impart a sense of this dynamism to the reader. Those wanting a broader overview of the LTSH for all the A-15's (of which there are over 50) are referred to the review by Weger and Goldberg, 1973, to two excellent theses on this subject from Professor Muller's group in Geneva (Spitzli, 1970 and Junod, 1974), and to a review of the LTSH of 25 superconducting A-15's in this conference by Dr. Junod, 1982a.

DISCUSSION

At low temperatures, but above any superconducting transition, the specific heat at constant pressure, C_p , is given by

The coefficient γ can be related to the electronic density of states at the Fermi level, $N(0)$, in units of states/eV-atom, and the electron-phonon coupling constant λ via

$$N(0)(1+\lambda) = 0.1061 \gamma \quad (2)$$

if γ is in units of mJ/mole-K² and a formula unit of the A-15 contains four atoms, i.e., A₃B. The coefficient β can be related to the Debye temperature, θ_D , which is a measure of lattice stiffness, via

$$\theta_D = \left(\frac{1944 \times 4}{\beta} \right)^{1/3} \times 10 \quad (3)$$

where β is in units of mJ/mole-K⁴. At higher temperatures, $\sim \theta_D/10$, even though δT^5 may be negligible in some materials, the Debye law for the lattice specific heat deviates from the simple βT^3 term in Eq. 1 causing a negative curvature on a C_p/T versus T^2 plot. For a complete discussion of the Debye law for the specific heats of solids, see Gopal, 1966. At low enough temperatures, the T^5 and higher order terms in Eq. 1 are negligible, and the simple Debye law is obeyed, allowing separation of γ and β by plotting C_p/T versus T^2 which gives γ as the intercept and β as the slope.

Already this discussion leads us to the controversy concerning LTSH measurements on the high T_C A-15's.

How Accurately Is γ Known for the Seven High T_C A-15's

The extrapolation of the normal state C_p data from above T_C to 0 K to determine γ for a high T_C superconductor is quite long and therefore subject to possible error. An example is shown in Fig. 1 where C_p/T versus T^2 is plotted from 4 to 29K for single phase A-15 Nb₃Ge, with a bulk T_C for this particular sample of 21.8K. There are no significant T^5 or higher order terms present in the data above T_C up to 29K, or $\theta_D/10$. As an aside, lack of such terms to such a large fraction of the Debye temperature is unusual in most materials. However, in the seven high T_C A-15 compounds under discussion here, such terms are absent in C_p above T_C up to $\theta_D/10$ in a majority of the cases, i.e., Nb₃Ge as we have seen and also Nb₃Al (Junod et al., 1971), Nb₃Al_{0.8}Ge_{0.2} (Stewart et al., 1978b), Nb₃Ga (Stewart and Webb, 1980) and Nb₃Sn (Stewart, et al., 1981a). As pointed out by Junod and Muller, 1980, and as will be seen below, merely because $C_p = \gamma T + \beta T^3$ above T_C up to $\theta_D/10$ for these materials is no assurance that βT^3 will continue to describe the lattice specific heat for $T < T_C$.

Returning to the question of how γ is determined for Nb₃Ge, the 42 data points above T_C were fitted by a least-squares computer program to $C_p/T = \gamma + \beta T^2$, with the result being $\gamma = 30.3$ mJ/mole-K² and $\theta_D = 302$ K. Now we arrive at the kernel of the controversy: how accurate are these numbers? The standard way to check is to use the fact that the normal state entropy at T_C , $S_N(T_C)$, equals the superconducting state entropy at T_C , $S_S(T_C)$, where C_N is the

$$S_N(T_C) = \int_0^{T_C} \frac{C_N}{T} dT = \int_0^{T_C} \frac{C_S}{T} dT = S_S(T_C) \quad (4)$$

extrapolated normal state data below T_C and C_S is the measured superconducting state data below T_C . For the Nb₃Ge data shown in Fig. 1, and using the straightforward extrapolation of the normal state data fit above T_C to $C_N/T = \gamma + \beta T^2$, the agreement of the entropies

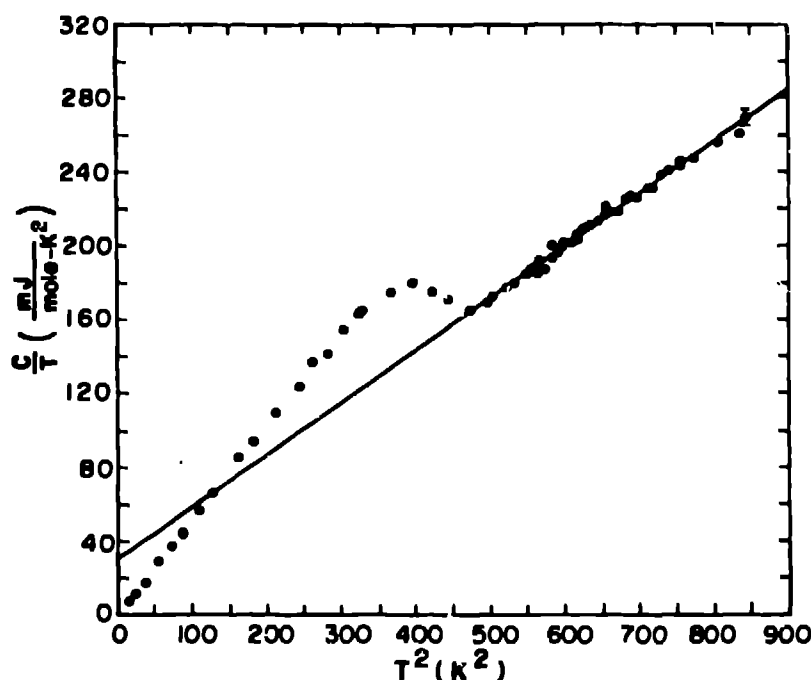


FIGURE 1. Low temperature specific heat (LTSH) data for single phase A-15 Nb_3Ge (Stewart et al., 1978a). The straight line shown is from a least-squares computer fit of the C_n/T data to $\gamma + BT^2$.

calculated via Eq. 4 is better than 1%. Thus, the γ for this sample of A-15 Nb_3Ge of 30.3 mJ/mole-K^2 is, in my opinion, quite reliable.

One can argue that if better material could be prepared (more homogeneous, less strained) the specific heat anomaly for Nb_3Ge would be sharper, instead of 3K wide, and perhaps γ would increase significantly in this better material. All the available evidence argues against this. One quite compelling piece of evidence is that better samples of Nb_3Al , with a much sharper specific heat anomaly at T_c have been measured and show less than a 10% change in γ (Cort et al., 1981). Also, band structure calculations by Klein et al., 1978, coupled with an approximate λ give, via Eq. 2, a γ for ideal A-15 Nb_3Ge a few percent lower than the number quoted here. (For a more complete discussion of this, see Stewart et al., 1979).

Nb_3Ge is only one of the seven high T_c A-15 compounds under discussion here. For how many others does the straightforward extrapolation discussed above work? Obviously, V_3Si and Nb_3Si are not straightforward, since the simple Debye law doesn't work for these compounds above T_c to begin with. Of the other four high T_c A-15's, only $\text{Nb}_3\text{Al}_{0.8}\text{Ge}_{0.2}$ is as straightforward as Nb_3Ge , with $\gamma = 35.0 \pm 2 \text{ mJ/mole-K}^2$ and 1% agreement of $S_s(T_c)$ and $S_n(T_c)$. Eq. 4 using $C_n(T < T_c)/T = \gamma + BT^2$.

For Nb_3Al and Nb_3Si , the γ 's obtained (Cort et al., 1981 and Stewart et al., 1981c respectively) to follow the entropy constraint and shown in Table I are only slightly different than those obtained from fits to the normal state data, which for Nb_3Si include a T^5 term.

TABLE I
PARAMETERS* FOR THE SEVEN HIGH T_C A-15's

	T_C (K)	γ (mJ/mole-K ²)	θ_D (K)	λ	$N(0)$ (states/eV-atom) experiment/theory
Nb ₃ Ge	21.8	30.3 \pm 1	302 \pm 3	1.7 \pm 0.2	1.2 \pm 0.1 / 1.0
Nb ₃ Ga	19.8	46 \pm 8	280(T=0) 262(T> T_C)	1.7 \pm 0.2	1.8 \pm 0.4 / 1.8
Nb ₃ Al	18.7	36 \pm 2	283 \pm 5	1.7 \pm 0.2	1.4 \pm 0.2 / 1.8
Nb ₃ Sn**	17.9	35 \pm 3	208(T=0) 270(T> T_C)	1.7 \pm 0.2	1.4 \pm 0.2 / 1.5
Nb ₃ Si	18.0	24 \pm 6	310 \pm 40	1.7 \pm 0.2	0.95 \pm 0.3 / 0.6
V ₃ Si**	17.1	52.8 \pm ?	271-304 (T=0) 435(T> T_C)	1.29 \pm 0.2	2.4 \pm 0.3 / 1.8
Nb ₃ Al _{0.8} Ge _{0.2}	20.0	35 \pm 2	278 \pm 5	1.7 \pm 0.2	1.4 \pm 0.2

*References are given in the text. **Values are for transforming samples.

The case of Nb₃Si, produced by explosive compression and available only as a multi-phase material, is somewhat complex. The uncertainty in the γ shown in Table I for A-15 Nb₃Si is totally due to uncertainties in correcting for the γ 's of the other phases, since Stewart et al., 1981c, suppressed T_C substantially using an applied magnetic field to accurately determine γ .

For Nb₃Ga, Stewart and Webb, 1980, assign a γ of 46 \pm 8 mJ/mole-K². Here, not only is $S_n(T_C)$ from a straightforward extrapolation in disagreement with $S_s(T_C)$, but there is also a second phase to be corrected for.

For V₃Si, as for Nb₃Sn, extrapolation of C_n below T_C is made difficult by the fact that $\theta_D(T > T_C)$ is significantly different than $\theta_D(T \ll T_C)$. For V₃Si, the values given by Junod and Muller, 1980, are $\theta_D(T > T_C) = 435$ K and $\theta_D(2\text{K} < T < 4\text{K}) = 271 - 304$ K, depending on sample. The low temperature Debye temperature is measurable because the electronic contribution to C_s becomes negligible sufficiently below T_C , leaving $C_s = \theta T^3$ as shown in Eq. 5.

$$C_s = Ae^{-A/kT} + \theta T^3 \quad (5)$$

Thus, because the Debye temperature in V₃Si is obviously temperature-dependent below T_C , the slope of the extrapolation of C_n/T vs T^2 is also changing in some fashion between 4K and T_C . Junod and Muller's choice for γ of transformed A-15 V₃Si is 52.8 mJ/mole-K² using a $\theta_D(T)$ which is based on the shape of the phonon spectrum $F(\omega)$. This number is at present disputed by Huang et al., 1981, who measure a low temperature specific heat smaller by a factor of two for their transforming V₃Si crystal than that obtained by Junod and Muller on four different samples and by Brock, 1969, on his sample. Since Huang et al. obtain a smaller C_s , they obtain a larger $\theta_D(T \ll T_C)$ of 425K, leading them to extrapolate γ for their transforming V₃Si as 67.6 mJ/mole-K². This 28% disagreement must be resolved by either an independent measurement of C_s at low temperatures on the Huang et al.

sample (as suggested by Junod, 1982b) or by a measurement of C_p for V_3Si in high magnetic fields (12-15T) to suppress T_c and actually measure C_n , rather than having to extrapolate it.

For Nb_3Sn , similar difficulties in extrapolation arise from a changing Debye temperature, $\theta_D(T < 4K) = 208K$ versus $\theta_D(T > T_c) = 270K$ (Stewart et al., 1981a). A straightforward extrapolation of the normal state data above T_c fitted to $C/T = \gamma + \beta T^2$ gives $S_n(T_c)/S_s(T_c) = 1.23$ for Nb_3Sn . However, since the change in θ_D from T_c to 4K makes it clear that such an extrapolation will, a priori, be incorrect, extrapolations have always been made to: 1) have the correct slope at $T = 0$; 2) give the correct $S_n(T_c)$ (i.e. $= S_s(T_c)$). Junod et al., 1978, based their extrapolation on $F(\omega)$ data from neutron scattering and obtained $\gamma = 46.8$ to 52.4 mJ/mole-K², depending on sample. Vieland and Wicklund, 1968, obtained $\gamma = 52.4$ mJ/mole-K² for their sample of Nb_3Sn based on data in 0 and 5.25T fields and an extrapolation using Hg as a model. Using Pb as a model gave a value 10% lower.

Recently, Stewart et al., 1981a, succeeded in measuring the LTSH of a high-quality, vapor-grown polycrystal of Nb_3Sn in a magnetic field high enough (18T) to allow measurement of C_n down to $T^2 = 40K^2$, a factor of three greater depression of T_c than that obtained by Vieland and Wicklund with 5.25T. This measured C_n gives a much more accurate extrapolation of $\gamma = 35 \pm 3$ mJ/mole-K². This result remains controversial because of two points. Firstly, of course, is that a γ of 35 vs the previously accepted value of 52 mJ/mole-K² requires a big adjustment in the perception of A-15 Nb_3Sn as a high density of states superconductor. Secondly, the high field C_n data show an abrupt change in θ_D at about 11K which is not seen in the zero field C_s data. While we pointed out several cases where data exist showing that applied fields can affect lattice behavior, this abrupt change in lattice stiffness in 18T in Nb_3Sn is as yet not understood. Experimental work is ongoing to measure the magnetoresistance in applied field of this same sample (Brandt et al., 1982) to see if another measurement can shed light on this anomaly. Also, theoretical work (Pickett and Klein, this conference) is underway to try to understand this anomaly.

Certainly the question of why this anomaly exists seems unanswered at the present time. Arguments which try to explain the abrupt change, or kink, in θ_D with temperature in 18T based on some slight remaining untransformed cubic material undergoing a superconducting transition at 11K are unconvincing for several reasons. First, the critical field at zero temperature of such cubic material would be over 30T. Such a high upper critical field has never been observed in Nb_3Sn . Second, a superconducting transition would increase the specific heat over a range of temperature, not cause it to drop precipitously as observed. Third, all these arguments are academic since this sample was measured inductively for superconductivity in 18T (Foner, 1981) and was found to be normal down to a significantly lower temperature.

At the present time, my belief is that γ for Nb_3Sn is 35 ± 3 mJ/mole-K². The size of the normalized specific heat discontinuity, $\Delta C/\gamma T_c$, which this gives (3.5 ± 0.3) is not any larger than that extrapolated for high-quality Nb_3Al , 3.2 (Cort et al., 1981). Now, more thorough, neutron diffraction should be done on high-quality Nb_3Sn to more completely determine $F(\omega)$. Of great significance would be such neutron work done in high fields.

Determination of $N(0)$; Comparison with Theory

Knowing γ now for the seven high T_c A-15's (see Table I) to various degrees of precision and with varying degrees of controversy, can we now use these values to calculate $N(0)$ from Eq. 2? Do we know λ ?

For three of the seven high T_c A-15's, tunneling measurements have been done which give a λ value: for Nb_3Ge , $\lambda = 1.7 \pm 0.15$ (Kihlstrom and Geballe, 1982); for Nb_3Sn , $\lambda = 1.55$ to 1.69 (Shen, 1972) vs $\lambda = 1.80$ (Rudman and Beasley, 1981); for sub-stoichiometric Nb_3Al with $T_c = 16.2K$, Kwo et al., 1981 give $\lambda = 1.65$. Far infrared studies (McKnight et al., 1979) on V_3Si give $\lambda = 1.29$. For the remaining three high T_c A-15's, we are reduced to using a phenomenological formula put forward by Rowell, 1976:

$$T_c = \frac{\theta_D}{20} (\lambda - 0.25) \quad (5)$$

For Nb_3Ga , using $T_c = 19.8K$ and $\theta_D = 280K$ (Stewart and Webb, 1980), Rowell's formula gives $\lambda = 1.66$. For $Nb_3Al_{0.8}Ge_{0.2}$, using $T_c = 20.0K$ and $\theta_D = 278K$ (Stewart et al., 1978b), Rowell's formula gives $\lambda = 1.69$. Due to the multiphase nature of the explosively prepared A-15 Nb_3Si sample whose LTSH was measured by Stewart et al., 1981b, θ_D for this A-15 is, as yet, ill-determined. By analogy to Nb_3Al , Stewart et al., 1981b, assigned $\lambda = 1.7$ for Nb_3Si .

These values for λ are listed in Table I. Clearly there is significant uncertainty attached to these numbers. Perhaps most fundamentally, tunneling measurements on these high T_c compounds only sample the properties of the material to a depth of less than 100 \AA . Thus, any surface imperfections (composition, strain, defects, impurities) will cause an erroneous value for λ to be obtained. Second, the value given above for sub-stoichiometric Nb_3Al ($T_c = 16.2K$) is likely lower than the correct value for the higher quality, $T_c = 18.7K$ material used in the specific heat studies. Third, the derivations of λ for Nb_3Ge and Nb_3Sn are based on assumptions that may in fact be incorrect. (For a discussion of these assumptions, see Wolf et al., 1980). Last, the use of Rowell's formula for Nb_3Ga and $Nb_3Al_{0.8}Ge_{0.2}$ must be viewed as only an approximation.

Therefore, error bars of ± 0.2 are used for the λ values listed in Table I to indicate their approximate nature. Even before we use Eq. 2 to calculate $N(0)$, we see a remarkable thing from Table I: except for V_3Si , γ and λ values for the high T_c A-15 compounds are all very similar.

The $N(0)$ values, again excluding V_3Si , range from a low value of 0.95 ± 0.3 states/eV-atom for Nb_3Si to 1.8 ± 0.4 states/eV-atom for Nb_3Ga . Except for V_3Si , all of the high T_c A-15 superconductors have $N(0)$ values less than that of Nb (2 states/eV-atom) which has a T_c of only $9.2K$. This is not a result inconsistent with recent band structure calculations by Klein et al., 1978. They found $N(0)$ (see Table I) varied from 0.64 states/eV-atom for Nb_3Si to 1.84 states/eV-atom for V_3Si .

It is thus quite clear that these high T_c A-15 compounds do not owe their elevated superconducting transition temperature to a high density of states value. The opinion to the contrary is still at large in the scientific community, dating back to the specific heat work of Morin and Maita, 1963. In this early work, totally erroneous values of 4.40 and 5.5 states/eV-atom were reported for Nb_3Sn and V_3Si respectively based on values of γ which were too high due to the lack of an entropy check. Also, the factor of $(1 + \lambda)$ in Eq. 2 was unknown at that time.

Hopefully this review article has served to dispel the false idea that high T_c implies high $N(0)$. As we have seen, it certainly is not true for the high T_c A-15 compounds. Additionally, the only other materials known with $T_c > 17.0K$ ($Y_{0.7}Th_{0.3}C_{1.35}$, $T_c = 17.0K$ and $Nb_{0.30}Nb_{0.70}$, $T_c = 17.4K$) have values for γ that are even lower than those discussed here for the high T_c A-15's: $\gamma = 4.7 \text{ mJ/mole-K}^2$ (Stewart et al., 1978c) and $\gamma = 3.3 \text{ mJ/mole-K}^2$ (Geballe et al., 1966)

However, saying that the high T_C A-15's do not owe their high T_C 's to a large density of states at the Fermi energy still leaves the puzzle of "Why high T_C ?" unanswered. Further experiments, and perhaps more importantly, fresh theoretical insight are still needed.

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